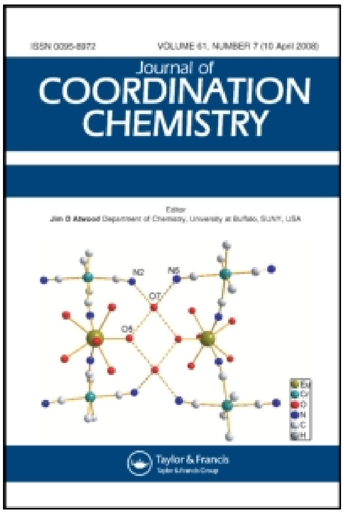

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THE BIS(o-AMINOTHIOFENOLATO)COBALTATE ION
A New Spin Triplet Co Species

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In the paramagnetic (3.25 BM) bis(o-aminothiofenolato)cobaltate ion $Co(abt)_2^-$, the central cobalt atom is coordinated with two sulfur and two nitrogen atoms. This complex ion has no affinity for further ligands, presumably due to a high electronic charge on the cobalt atom, induced by the very strong electron donating ligand system. This is in accordance with a very low reduction potential being intermediate between those of analogous N_4 and S_4 coordinated complexes. The chemical and electrochemical properties of this and other spin triplet cobalt complexes are compared with each other.

INTRODUCTION

A number of four-coordinated spin triplet cobalt complexes has been reported: several mononegative bis(dithiolato)cobaltate ions containing planar S_4-coordinated cobalt atoms,[1,2] the bis(o-mercaptofenolato)cobaltate ion $Co(mp)_2^-$,[3] with a presumably planar S_2O_2-coordination and the planar N_4-coordinated (biuretato)cobaltate complexes.[4,5] The paramagnetic $S = 1$) compound $[Co\{(C_6H_{11})_3PO\}_2I_2]I$ has been reported,[6] in which the cobalt atom is presumably planar coordinated. Besides there are two five-coordinated spin triplet cobalt complexes: the trigonal bipyramidal $Co[(C_2H_5)_3P]_2Cl_3$[7] and the square pyramidal cobalt complex of 1,2-bis-(o-iminobenzylideneamino)-propaan, Co(abpn)Cl.[8] We now report about the synthesis and properties of a new N_2S_2-coordinated spin triplet cobalt complex (Figure 1). Its chemical and electrochemical properties are compared with those of other planar spin triplet cobalt complexes.

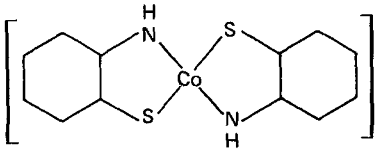

FIGURE 1 The $Co(abt)_2^-$ ion.

EXPERIMENTAL

Preparation of $(n\text{-}C_4H_9)_4NCo(C_6H_4SNH)_2$, $bu_4NCo(abt)_2$: In 25 ml of absolute ethanol 1.20 g of potassium metal (0.03 mol) was dissolved. Under nitrogen 1.84 g of o-aminothiofenol (0.014 mol) were added and after 5 minutes a solution of 1.60 g of $CoCl_2 \cdot 6H_2O$ (0.007 mol) dissolved in 10 ml of absolute ethanol, immediately followed by a solution of 2.40 g (0.0074 mol) of $(n\text{-}C_4H_9)_4NBr$ in 20 ml of absolute ethanol. Then the reaction mixture was stirred for a few seconds in air. The suspension was cooled down to −10°C. The precipitate was filtered off and washed with 100 ml of cold absolute ethanol and dry ether until the filtrate was colourless. The precipitate was then dissolved in 100 ml of dry, warm dichloromethane. This blue solution was filtered and concentrated to a volume of about 20 ml under vacuum. The pure complex was then precipitated by adding dry ether, filtered off and washed with ether.

Anal. Calcd. for $bu_4NCo(abt)_2$: C, 61.40; H, 8.47; N, 7.67; Co, 10.8. Found: C, 61.47; H, 8.65; N, 7.65; Co, 10.7.

By the same procedure $(C_2H_5)_4NCo(abt)_2$ could be prepared using 1.36 g of $(C_2H_5)_4NBr$ instead of 2.40 g of $(n\text{-}C_4H_9)NBr$.

PHYSICAL MEASUREMENTS

Electronic spectra were recorded on a Unicam SP800 spectrofotometer. Magnetic susceptibilities were

TABLE I
The UVV spectrum of $bu_4NCo(abt)_2$ in various solvents. Some major bands; extinction coefficients in parentheses.

Solvent	ν_1(kK)	ν_2(kK)	ν_3(kK)
DMSO	14.4 (7700)	17.8 (15900)	25.4 (6320)
DMSO + $C_3H_7NH_2$	14.4	17.8	25.4
Pyridine	15.0	17.5	25.1

measured on a Gouy type equipment. Polarographic data of abt- and toluenedithiolato(tdt)-complexes were obtained with a Metrohm Polarecord E261 and a E446 iR compensator. The measurements were carried out in DMSO with a rotating platinum electrode *vs* a saturated calomel electrode and 0.1N bu_4NClO_4 as supporting electrolyte.

RESULTS

The blue paramagnetic complex $bu_4NCo(abt)_2$ has an effective magnetic moment of 3.25 BM indicating a spin triplet state. The magnetic susceptibility obeys the Curie-Weiss law over a temperature range of –150 to +20°C (θ = –20°) (Figure 2). For $Co(tdt)_2^-$ a singlet ground state has been suggested.[14] We plan to investigate the magnetic properties of $bu_4NCo(abt)_2$ at very low temperatures to see if the triplet state is the ground state as has been shown for the (biuretato)cobaltate(III) complexes.[5]

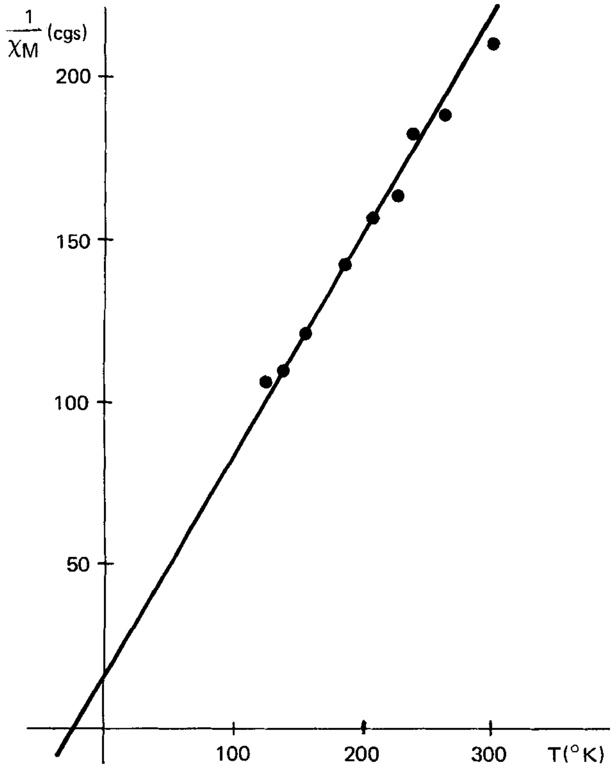

FIGURE 2 The temperature dependence of the magnetic susceptibility of $bu_4NCo(abt)_2$ (corrected for diamagnetism).

The complex can be reversibly reduced in a one-electron step. The polarographic $E_{1/2}$ value for reduction of this S_2N_2-coordinated complex is –1.27V. $E_{3/4} - E_{1/4}$ = 58 mV at 25°C; the theoretical value for a reversible one electron reduction is 56 mV at 25°C. This $E_{1/2}$ value is intermediate between those of the analogous S_4 and N_4 coordinated cobalt complexes, measured under the same conditions:

$$Co(CH_3{-}C_6H_3S_2)_2^-\ E_{1/2} = -0.83V$$
$$Co(o{-}C_6H_4(NH)_2)_2^-\ E_{1/2} = -1.83V^{10}$$

The UVV spectrum is hardly altered going from a DMSO to a pyridine solution, indicating that there is no affinity for further ligands (Table I). In the IR spectrum only one NH stretching frequency is observed. This indicates that the complex ion probably has a trans configuration (C_{2h}), as in the cis configuration (C_{2v}) two NH stretching frequencies are expected. This can easily be shown by group theoretical arguments.

DISCUSSION

The paramagnetic $Co(abt)_2^-$ ion is another representative of a series of paramagnetic ($S = 1$) cobalt complexes. In view of the fact that these complexes can be prepared with rather different ligand systems, it seems that the spin triplet ground state is fairly normal for Co in an environment that has a symmetry lower than O_h.

In the spin triplet compounds $[Co\{(C_6H_{11})_3PO\}_2I_2]I$, $Co[(C_2H_5)_3P]_2Cl_3$ and the bis(biuretato)cobaltate ion, Co can be denoted as being in the formal oxidation state III. Extended Hückel calculations have revealed that in the bis(biuretato)cobaltate ion the d orbitals of Co are unmixed with ligand orbitals, so that the electron configuration d^6 is an appropriate description of the

TABLE II
Properties of spin triplet cobalt complexes.

Compound	$E_{1/2}$ in DMSO RPE *vs* SCE	Reaction with: Amines	Triphenyl phosphin	Diamagnetic in solid state
$bu_4NCo(abt)_2$	−1.27[c]	no[c]	no[c]	no[c]
$bu_4NCo(CH_3-C_6H_3S_2)_2$	−0.83[c]	no[1,13]	no[c]	no; monomer(2)
$KCo(3\text{-prbi})_2(1\text{-prbiH}_2)_2$[a]	−0.71[5]	yes[5]	no[c]	no; monomer(4)
$bu_4NCo(mp)_2$	−0.62[3]	yes[3]	yes[3]	no[3]
$bu_4NCo(o\text{-phenbi}_2)$[b]	−0.47[5]	yes	yes[c]	no[5]
$bu_4NCo(Cl_4C_6S_2)_2$		yes[9]	yes[13]	yes; dimer[9]
$bu_4NCo((CN)_2C_2S_2)_2$	−0.05[12]	yes[1]	yes[11]	yes[1]

[a] $3\text{-prbi} = (HN-CO-N(C_3H_7)-CO-NH)^{2-}$. $1\text{-prbiH}_2 = H_2N-CO-NH-CO-NHC_3H_7$.
[b] $o\text{-phenbi}_2 = [o-C_6H_4(N-CO-NH-CO-NH)_2]^{4-}$.
[c] own observation.

electronic state of the metal.[5] However, in the newly prepared compound as well as in the dithiolato and mercaptofenolato complexes the oxidation state of Co cannot be uniquely defined and the bonding of the metal may have appreciable covalent character. Nevertheless some properties of these complexes agree nicely with those of the biuretato complex. The relation between $E_{1/2}$, magnetic properties and the reaction with amines or phosphines to diamagnetic 6- or 5-coordinated species is illustrated in Table II. A low $E_{1/2}$, a low electrophilicity and the persistence of paramagnetic monomers in the solid state obviously go together. These properties strongly suggest a relatively high electronic charge on the central metal atom that must be induced by the ligand system. We think that very strong electron donation is one of the main properties required to stabilize these low symmetry cobalt complexes. Once that four or five coordination is stabilized, there is a fair chance that such a complex is in a spin triplet state. The only limiting factor in preparing these spin triplet compounds seems to be the small number of ligands that stabilize these geometries.

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